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TRANSPARENT FLEXIBLE POLYOLEFIN COMPOSITION

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TRANSPARENT FLEXIBLE POLYOLEFIN COMPOSITION

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SPECIFICATION

1. Title of Invention

Transparent Flexible Polyolefin Compositions

2. Claim

Transparent flexible polyolefin compositions consisting of Components A and B which are defined below.

Component A Ethylene-vinyl acetate copolymer, the latter constituting
10-35 wt% of the component 20-95 wt%

Component B Binary (ethylene-propylene) elastomer and/or ternary (ethylene-propylene-unconjugated diene) elastomer 80- 5 wt%

[Component B being characterized by the following features:

Propylene content 10-20 wt%

Gel fraction (after 48 hours in cyclohexane at 30°C) 10-60 wt%]

2. Detailed Explanation of the Invention

This invention concerns certain transparent and flexible polyolefin compositions formed by blending specific ethylene-vinyl copolymer resins with specific ethylene-propylene type copolymers.

Copolymer resins of ethylene and vinyl acetate exhibit outstanding flexibility, impact strength and transparency and are widely used for molded products in which the above characteristics are desired.

In attempts to confer additional features while retaining the meritorious properties described above, there have been a number of recent proposals for blending ethylene-vinyl acetate copolymers with other elastomers.

Examples of proposed compositions include combinations of ethylene-vinyl acetate elastomer with butadiene-styrene elastomer and polybutadiene to enhance blocking (Japanese Patent Publication 44-26552) and with ethylene-propylene elastomer, filler and crosslinking agent to obtain a flexible crosslinking insulating

material (Japanese Patent Publication 49-12331).

Ethylene-propylene elastomer is representative of rubber-like polymers. A number of compositions of this material with ethylene-vinyl acetate copolymer have been suggested. Thus far there has been no report of a composition which exhibits high transparency. In fact, the addition of another elastomer has been found to markedly reduce the transparency of ethylene-vinyl acetate.

These elastomer compositions, therefore, have had little utility when transparency was especially desired.

After much effort to develop an elastomer composition of good transparency, we discovered that when ethylene-vinyl acetate copolymer resin containing 10-35 wt% vinyl acetate was combined with a suitable amount of ethylene-propylene type of copolymer containing 10-20 wt% propylene and forming 10-60 wt% gel fraction after 48 hours in cyclohexane at 30°C, polyolefin compositions characterized by flexibility, good recovery after stress and, above all, transparency of a degree heretofore not achieved were obtained.

This invention concerns some transparent and flexible polyolefin compositions consisting of Components A and B which are defined as follows.

<u>Component A</u>	Ethylene-vinyl acetate copolymer (10-35 wt% vinyl acetate:	20-95 wt%
<u>Component B</u>	Binary (ethylene-propylene) elastomer and/or ternary (ethylene-propylene-unconjugated diene) elastomer	80- 5 wt%

[Component B being characterized by the following features:

Propylene content	10-20 wt%
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Gel fraction after 48 hrs in cyclohexane at 30°C)	10-60 wt%
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When the composition is prepared from ethylene-vinyl acetate copolymer containing less than 10 wt% vinyl acetate and an ethylene-propylene elastomer satisfying the specifications of this invention, the transparency is the same as that of conventional products, and moreover there is inadequate flexibility. Conversely, when the ethylene-vinyl acetate fraction is prepared in accordance with our invention but the ethylene-propylene elastomer is not prepared according to our prescription, flexibility and recovery after stress are quite satisfactory but transparency is extremely poor.

On the basis of these experiences, it was quite unexpected that a combination of ethylene-vinyl acetate copolymer and ethylene-propylene elastomer should result in a composition of high transparency.

The composition obtained by the method of our invention has the above-described merits (flexibility, mechanical strength, recovery from fatigue, impact strength and blocking resistance) as well as greatly increased transparency, so that it is applicable to a wide range of uses (especially as material for film wrappers

and blown containers).

The content of vinyl acetate in Component A should be 10-35 wt%, preferably 10-30 wt%. When it is below 10 wt%, the product (blend of ethylene-vinyl acetate and ethylene-propylene elastomer) lacks flexibility, while an excess (over 35 wt%) of vinyl acetate results in poor heat resistance and surface stickiness.

The ethylene-vinyl acetate copolymer should have a melt flow rate (MFR, measured at 190°C) of 0.1-30 g/10 min. It is prepared by high-pressure polymerization. A suitable commercial product may be used.

Component B is a random copolymerization product obtained by the use of a Ziegler-Natta type of catalyst. The content of propylene should be 10-20 wt%, preferably 15-20 wt%, and the gel fraction after 48 hours in cyclohexane at 30°C should be 10-60 wt%, preferably 20-60 wt%. Component B may be a binary (ethylene-propylene) elastomer (EPM) or a ternary (ethylene-propylene-unconjugated diene) elastomer (EPDM).

When the propylene content is under 10 wt%, the composition lacks flexibility and stress recovery, and when the content of propylene exceeds 20 wt%, the product lacks transparency.

Similarly when the gel fraction is less than 10 wt% the product lacks transparency, and when the gel fraction exceeds 60 wt% the composition is deficient in flexibility and stress recovery.

Gel fraction is the proportion of insoluble fraction to the original weight when the material has been immersed for 48 hours in cyclohexane at 30°C. The determination is conducted as follows.

(1) To 100 ml cyclohexane, 0.25 g of sample (cut into pieces about 1 mm square) is added.

(2) The preparation is allowed to stand for 48 hours at 30°C.

(3) The material is passed through an 80-mesh wire screen and the amount retained by the screen is measured and the gel fraction is calculated.

Ethylene-propylene elastomers are known as EPM or EPDM. A commercial product may be used so long as it satisfies the requirements regarding propylene content and gel fraction.

Examples of unconjugated dienes used in EPDM are 1,4-hexadiene, dicyclopentadiene, methylene-norbornene, ethylidene-norbornene and propenyl-norbornene. The content is generally under 15 wt%.

The proportionality of Components A and B relative to the total weight should be 20-95, preferably 40-90, wt% Component A, the rest being Component B. When the content of Component A is under 20 wt% the product is deficient in moldability, visual attractiveness and mechanical strength, and when the content is in excess of 95 wt% there is loss of elasticity.

The composition of our invention consists essentially of Components A and B, although certain other ingredients may be present. These include a small amount of resin or elastomer which is compatible with at least one of the essential components (the content of the third component should not exceed 30 wt%) and auxiliary substances generally used with this type of resin or elastomer, such as stabilizer, plasticizer, oil, foaming agent and filler. Since the feature of the composition of our invention is transparency, the third component and auxiliary materials must not significantly compromise that property.

The composition of our invention is, of course, characterized by not only transparency but also flexibility, moldability, outward attractiveness, blocking resistance, and mechanical strength (impact and tensile). Attainment of these features must be balanced against that of transparency.

Transparency is perceived when the haze value (obtained using the procedure to be described on pressed sheets 1 mm in thickness) is under 70%, but the starting material in our invention is ethylene-vinyl acetate copolymer which is highly transparent (haze value of under 10%), so that upon combination with ethylene-propylene elastomer there is inevitably a marked loss of transparency. Even so, the composition of our invention is quite transparent, the haze value being generally under 40%.

For the preparation of the composition consisting of Components A and B, any known method of blending of thermoplastic resin with elastomer may be used. The device used may be a monoaxial or a biaxial extruder, roller or Banbury mixer. When the elastomer (Component B) portion is small, a molded product may be produced directly by processing a dry blend by extrusion, hollow or injection molding.

The invention is explained in greater detail in the examples which follow.

Examples

1) Test procedure

- (1) MFR [g/10 min]: ASTM-d-1238 (190°C, load of 2.16 kg)
- (2) Density [g/cm³]: JIS-K-6760 (density gradient tube, 23°C)
- (3) Mooney granularity [-]: JIS-K-6300 (ML 1+4, 100°C)
- (4) Gel fraction [wt%]: Insoluble fraction after 48 hrs in cyclohexane at 30°C
- (5) Haze [%]: JIS-K-6714 (integrated light transmission measuring device)
- (6) Hardness [-]: JIS-K-6301 (A form)
- (7) Permanent extension [%]: JIS-K-6301, #3 dumbbell-shaped sample is drawn by 100% (to twice the length) and allowed to contract abruptly without snapping, and measuring the length 10 minutes later to determine residual extension.
- (8) Tensile strength [kg/cm²]: JIS-K-6301 (tensile velocity 500 mm/min, #3 dumbbell)

(9) Tensile strength [%]: JIS-K-6301 (tensile velocity 500 mm/min, #3 dumbbell

2) Resins and elastomers

(1) EVA-1 (Yukalon HE 60, a product of Mitsubishi Petrochemicals)

Vinyl acetate content 5 wt%

Density 0.93 g/cm³

MFR 0.5 g/10 min

(2) EVA-2 (Yukalon EVA 41H, a product of Mitsubishi Petrochemicals)

Vinyl acetate content 16 wt%

Density 0.94 g/cm³

MFR 2.0 g/10 min

(3) EVA-3 (Yukalon EVA-V 505, a product of Mitsubishi Petrochemicals)

Vinyl acetate content 25 wt%

Density 0.95 g/cm³

MFR 2.0 g/10 min

(4) EVA-4 (Yukalon EVA-X700, a product of Mitsubishi Petrochemicals)

Vinyl acetate content 33 wt%

Density 0.96 g/cm³

MFR 30 g/10 min

(5) EP-1 (EP-07P, a product of Mitsubishi Petrochemicals)

EPM

Mooney viscosity 70 [-]

Propylene content 25 wt%

Gel fraction 20 wt%

(6) EP-2 (experimental EPT, made by Mitsubishi Petrochemicals)

EPDM

Mooney viscosity 83 [-]

Propylene content 19 wt%

Gel fraction 23 wt%

3d component Ethylidene-norbornene

(7) EP-3 (Nordel 1500, a product of Du Pont Co.)

EPDM

Mooney viscosity 97 [-]

Propylene content 17.7 wt%

Gel fraction 0.50 "

3d component 1,4-hexadiene

3) Blending and sample preparation

(1) Blending

Apparatus: Brabender plastograph

Conditions: Rotation velocity 50 rpm
 Blending time 5 minutes
 Blending temperature 130°C

(2) Sample preparation

Apparatus: Compression molder

Conditions: Preheating: 150°C/0 kg (contact)/2 min

Pressure: 150°C/100 kg/3 min

Cooling: Running water/150 kg/1 min

Sample: Pressed sheet 1 mm in thickness

Control 1

The blend was that of ethylene-vinyl acetate resin containing more than 10 wt% vinyl acetate (EVA-2, EVA-3, EVA-4) and ethylene-propylene elastomer containing more than 20 wt% propylene (EP-1). Samples 1-5 prepared from this type of blend exhibited satisfactory flexibility (hardness) and stress recovery (permanent extension) but transparency was poor at 70-86%.

The results are shown in Table 1.

Note) At haze values of under 70%, the view on the other side of the pressed sheet of 1 mm thickness could be seen clearly with the unaided eye. At 70-85% there was considerable fog and the object was indistinct. At 85% and above the film became completely non-transparent and the object was invisible.

Table 1

Composition Items evaluated		Experiment No.				
		1	2	3	4	5
Resin	EVA-2	80	60	-	-	-
	EVA-3	-	-	80	60	-
	EVA-4	-	-	-	-	60
Elastomer	EP-1	20	40	20	40	40
Items evaluated	Haze (%)	78	77	70	73	86
	Hardness (-)	88	86	-	-	-
	Permanent extension (%) ₂	30.3	23.0	-	-	-
	Tensile strength (kg/cm ²)	140	99	-	-	-
	Tensile extension (%)	750	750	-	-	-

Example 1

Using a blend of ethylene-vinyl acetate used in Control 1 and a specific preparation of ethylene-propylene elastomer (EP-2, EP-3), samples 6-11 were prepared. All showed haze levels below 34%, indicative of transparency incomparably superior to that obtained in Control 1. Other properties included good flexibility (hardness in the 80's) and good stress recovery (permanent extension of around 30%).

Especially with EVA-3 and EVA-4 blends containing high levels of vinyl acetate, excellent transparency (haze values of 10-20%) was obtained.

The results are shown in Table 2.

		Table 2					
		Experiment No.					
Composition	Items Evaluated	6	7	8	9	10	11
Resin	EVA-2	80	60	-	-	-	-
	EVA-3	-	-	80	60	60	-
	EVA-4	-	-	-	-	-	60
Elastomer	EP-2	-	-	-	-	40	-
	EP-3	20	40	20	40	-	40
Items Evaluated	Haze (%)	34	33	15	10	20	16
	Hardness (-)	88	86	86	-	-	-
	Permanent extension (%)	32.5	30.8	28.0	-	-	-
	Tensile strength (kg/cm ²)	165	184	220	-	-	-
	Tensile extension (%)	775	788	775			

Control 2

In this control example, the ethylene-propylene elastomer was either EP-3 which satisfied the requirement of this invention or EP-1, the material used in Control 1, blended with ethylene-vinyl acetate resin containing less than 10 wt% vinyl acetate (EVA-1). The products (samples 12-15) were evaluated as in the above examples. It was found that the blends of EP-3 and EVA-1 (Experiment Nos. 14, 15) exhibited good transparency and stress recovery but poor flexibility (hardness of over 90), while the blends of EP-1 with EVA-1 (Experiments 12, 13) showed unexpectedly good transparency but poor flexibility (hardness of over 90).

The results are shown in Table 3.

Table 3

Experiment No.					
Composition Items Evaluated		12	13	14	15
Resin	EVA-1	80	60	80	60
Elastomer	EP-1	20	40	-	-
	EP-3	-	-	20	40
Items Evaluated	Haze (%)	9.0	8.5	10.3	25
	Hardness (-)	95	91	97	93
	Permanent ex- tension (%)	25.5	21.8	31.8	-
	Tensile strength (kg/cm ²)	163	149	214	-
	Tensile exten- sion (%)	825	900	812	-